Indian J. Phys. **72B** (6), 623-630 (1998)

IJP B
an international journal

Photoquenching effect in rigid (cresyl violet) and non-rigid (disodium fluorescein) dye molecules

George C Chennattucherry*, G Ajith Kumar, P R Biju, C Venugopal and N V Unnikrishnan

School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam-686 560, Kerala, India
*Department of Physics, St Berchmans' College, Changanacherry-686 101, Kerala, India

Received 19 May 1997, accepted 13 July 1998

Abstract The kinetic analysis of photoquenching in CV (cresyl violet)and FDS (disodium fluorescein) dye molecules has been performed in the light of the experimental results already reported It is found that there exists an optimum pump power which depends on the dye molecular characteristics Computer calculations have also been made under optically thin approximation to analyze the temporal behavior of gain and variation of efficiency on pump power This approach enabled us to distinguish between rigid and non-rigid dye systems

Keywords Photoquenching, dye laser, optically thin approximation

PACS Nos. 42.55 Mv, 33.50 Dq, 33 50 Hv

1. Introduction

Dye lasers have become a very important tool in laser research and laser applications. The advent of the N_2 laser and its successful use in pumping a dye laser [1] renewed the interest in pulsed laser pumped dye laser (PLPDL) systems because of their superior performance as far as the repetition rates and pulse durations are concerned. The theoretical studies on flash lamp or CW laser pumped dye laser systems have taken into account the triplet state formation, since it is a very important factor for determining the optimum conditions[2,3]. However, in the case of pulsed dye laser systems with short pump duration, triplet state formation is not significant. Here, excited singlet state absorption may become important and compete with laser emission from this state, thereby decreasing the fluorescence quantum yield. This effect, named photoquenching was analyzed kinetically by speiser *et al* [4]. Following their analysis, we have recently studied the fluorescence quenching in 7-dimethyl amino 4-methyl coumarin (7-DAMC) and rhodamine6-G dye molecules and quantitatively explained the dependence of quantum yield on the pulse and dye molecular characteristics [5]. In this paper we theoretically

reanalyzed the experimental findings reported by Gaur *et al* [6] in terms of the gain factor, threshold pump intensity, efficiency parameter etc. For this purpose, we adopt the coupled differential equation analysis for the ground and excited state population given by Speiser [7]. The pump power *vs* gain yields various molecular parameters for cresyl violet (CV) and disodium fluorescein (FDS) molecules. The analysis shows that CV is ideal for better quantum yield. The temporal behavior of gain reveals the rigid and non-rigid behavior of CV and FDS dye systems respectively.

2. Pump power dependence of gain

Under an optically thin approximation the steady state gain is given by [7]

$$G = \frac{N k_{21}[\sigma_{01}(p)(\sigma_e - \sigma_{12}(L)) I_p - \sigma_{01}(L)/\tau]}{[\sigma_{01}(p)\sigma_{12}(L) I_p^2 + k_{21}\sigma_{01}(p) I_p + k_{21}(1/\tau + \sigma_e I_L)]} - r \,. \tag{1}$$

The parameters have their usual meanings as in [7].

For a small gain dye amplifier, $\sigma_e I_L << 1/\tau$ and $r = 0$. If photoquenching effect are neglected $\sigma_{12} I_p = \sigma_{12}(L) I_L = 0$, then from eq. (1) we obtain,

$$G = N\left[\frac{(\sigma_e + \sigma_{01}(L))\sigma_{01} I_p}{\sigma_{01} I_p + 1/\tau} - \sigma_{01}(L)\right]. \tag{2}$$

This equation predicts a saturation like behavior when $\sigma_{12} I_p >> 1/\tau$. The saturated gain value is $G_{sat} = N\sigma_e = \alpha_e$.

If we take into account photoquenching effect we note that (1) does not predict saturation of the gain. In fact, a maximum for the gain is obtained which for $\sigma_e >> \sigma_{01}(L)$ occurs at pump intensities $I_p(\max)$ for which the fluorescence yield is maximum.

$$I_p(\max) = (k_{21}/\tau\sigma_{01}\sigma_{12})^{1/2} \,, \tag{3}$$

hence the optimum gain of a dye laser system can be determined from a study of its intensity dependent quantum yield.

We now reanalyzed the experimental data of Gaur *et al* [6] and try to fit them to (1) and (2). The experimental data are for dye systems disodium fluorescein (FDS) and cresyl violet (CV) at 337.1nm. It is observed from the gain *vs* pump intensity curves (Figures 1 and 2) that the gain decreases at higher pump intensity in both the dyes. Also, the maxima of FDS is at lower pump intensity as compared to that of CV. The drop in the gain value in the case of FDS at higher pump intensity is found much more as compared to that of CV.

The observed difference in variation of gain with intensity in the two cases may be attributed to the twisted intramolecular charge transfer (TICT) which are formed only in non-rigid dyes in their excited states [8, 9]. In this case, the pump energy after a certain value is largely used in twisting the molecules and hence nonradiative. Hence, the comparison of gain *vs* pump intensity curves of FDS and CV indicates that FDS is a non-rigid dye whereas CV is a rigid dye. The long range polarization interaction between solvent molecules and ion radical pair strongly stabilizes the latter and makes the electron transfer step energetically favourable The twist induces a large charge separation along the molecular skeleton between the donor

group and the acceptor moiety. Mobility of the amino groups enhances the charge separation by twisting the CN bond forming a TICT state. In rigid dyes, the possibility of TICT formation is very small because the rigid structure inhibits rotation about the CN bond, thereby preventing TICT formation. In non-rigid dyes, the dipole moment increases by a large amount during the twisting mechanism and these states are stabilized by the long range specific polarization interaction with solvent molecules. Other photophysical effects like bleaching and dye degradation under UV excitation may also cause a drop in the gain.

3. Temporal dependence of gain

The analysis of the temporal behavior of gain was proposed for an optically thin sample at a molecular concentration (N), transversely pumped by a laser pulse [10]. The rate equations for the molecular concentration in S_0, S_1 and S_2 and for the coupled dye laser intensity are

$$dN_0 / dt = -[\sigma_{01}(p)I_p + \sigma_{01}(L)I_L]N_0 + (1/\tau + \sigma_e I_L)N_1 , \tag{4}$$

$$dN_1 / dt = [\sigma_{01}(p)I_p + \sigma_{01}(L)I_L]N_0 - [1/\tau + \sigma_e I_L + \sigma_{12}(P)I_p + \sigma_{12}(L)I_L]N_1 + k_{21}N_2 , \tag{5}$$

$$dN_2 / dt = [\sigma_{12}(p)I_p + \sigma_{12}(L)I_L]N_1 - k_{21}N_2 , \tag{6}$$

$$dI_1 / dt = (c/\eta)[\sigma_e N_1 I_L - \sigma_{01}(L)N_0 I_L - \sigma_{12}(L)N_1 I_L + N_1 / p\tau] - I_L / t_c , \tag{7}$$

where

$$p = 8\pi\nu^2 \Delta\nu\, V / c^3$$

is the number of modes coupled to the fluorescence linewidth, $\Delta\nu$ centered around ν for a cavity of volume V [11].

$t_c = \eta\, l/c(1-r)$ is the photon lifetime in the cavity, l is the cavity length (equal to the length of the dye cell), r is the mirror reflectivity, c the velocity of light and η the refractive index of the medium.

$N_1/p\tau$ represents the spontaneous emission noise which is essential for initiation of the laser action. In solving (4-7) the following transformation to dimensionless quantities have been made.

$$A = \tau\sigma_{01}(p)I_p,\ Y = \tau\sigma_{01}(L)I_L,\ \theta = t/\tau,\ B = \tau\sigma_{01}(p)cN/\eta ,$$

$$\alpha = \sigma_e / \sigma_{01}(p),\ \beta = \sigma_{12}(p)/\sigma_{01}(p),\ \tau_c = t_c / \tau , \tag{8}$$

$$\gamma_1 = \sigma_{01}(L)/\sigma_{01}(p),\ \gamma_2 = \sigma_{12}(L)/\sigma_{01}(p),\ \gamma_3 = \tau k_{21},$$

$$X_0 = N_0 / N,\ X_1 = N_1 / N,\ X_2 = N_2 / N,\ N = N_1 + N_2 + N_3 ,$$

$$dX_0 / d\theta = -[A + \gamma_1 Y]X_0 + [1 + \alpha Y]X_1 , \tag{9}$$

$$dX_1 / d\theta = [A + \gamma_1 Y]X_0 - [1 + \alpha Y + \beta A + \gamma_2 Y]X_1 + \gamma_3 X_2 , \tag{10}$$

$$dX_2 / d\theta = [\beta A + \gamma_2 Y]X_1 - \gamma_3 X_2 , \tag{11}$$

$$dY / d\theta = B[\alpha Y X_1 - \gamma_1 Y X_0 - \gamma_2 Y X_1 - X_1 / p] - Y / \tau_c . \tag{12}$$

Generally in dye system, the $S_1 \rightarrow S_2$ absorption process induced by the pumping laser is dominant. Eqs. (9) to (12) were solved by fourth order Runge-Kutta method. In the calculations a Gaussian pulse shape having a duration of t_p at 1/e point was assumed for the exciting laser pulse.

$$I_p = I_p(0)\exp[-t/t_p)^2] = A(0)\exp[-(\theta/\tau_p)^2], \quad (13)$$

where $\tau_p = t_p/\tau$.

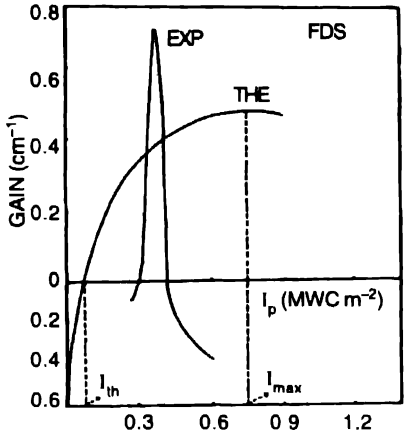

Figure 1 Gain *vs* Pump power for FDS (10^{-3} M) Both the experimental (exp) and theoretical (the) curves are shown

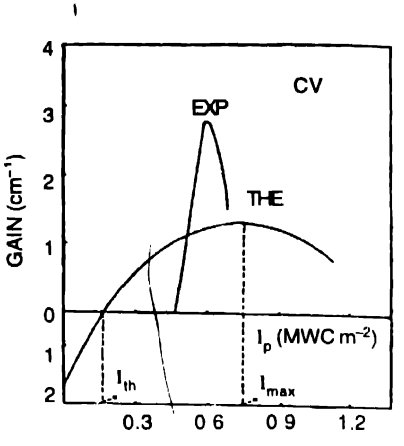

Figure 2 Gain *vs* Pump power for CV (10^{-3} M) Both the experimental (exp) and theoretical (the) curves are shown

For each set of molecular parameters for CV and FDS, pump characteristics and cavity variables, solutions are obtained for N_0, N_1, N_2 and I_L and for the gain function G defined by

$$G = (1/I_L)\,d\,I_L/d\,z = (\eta/cI_L)\,d\,I_L/d\,t = (\eta/\tau cY)\,dY/d\theta, \quad (14)$$

where z denotes the dye laser axis along which the fluorescence is measured.

Using eq. (14), the temporal dependence of G and I_L was calculated for FDS and CV under optically thin approximation. The transient gain shows completely different features for the two dye systems (Figure 3). The curve for FDS shows two peaks separated by a minimum A maximum is observed just before the pump reaches its peak intensity followed by a drop in the gain. The gain follows the population difference X_1-X_0 and when dye laser action starts X_1-X_0 decreases rapidly because of stimulated emission and the gain also drops. However, when photoquenching is important the gain does not decrease significantly ; since even after the pumping pulse, S_1 continues to be populated from S_2 and the gain may even reaches a second maximum.

In the case of CV, only one peak is observed. It is noted that the threshold pump intensity is higher for CV than for FDS. These phenomenon underlines the rigid structure of CV and non-rigid structure of FDS. The appearance of such peaks in the case of gain *vs* wavelength curve has already been observed experimentally [8] and is attributed to the rigid and non-rigid structure of CV and FDS respectively. Figures 4 and 5 show the dependence of gain function G (eq. 14) on A (eq. 8) for FDS and CV respectively at 10^{-3} M concentration. The peak gain of

FDS is observed to be at lower pump intensity as compared to that of CV. Also, the drop in the gain value in the case of FDS at higher pump intensity is found much more as compared to that

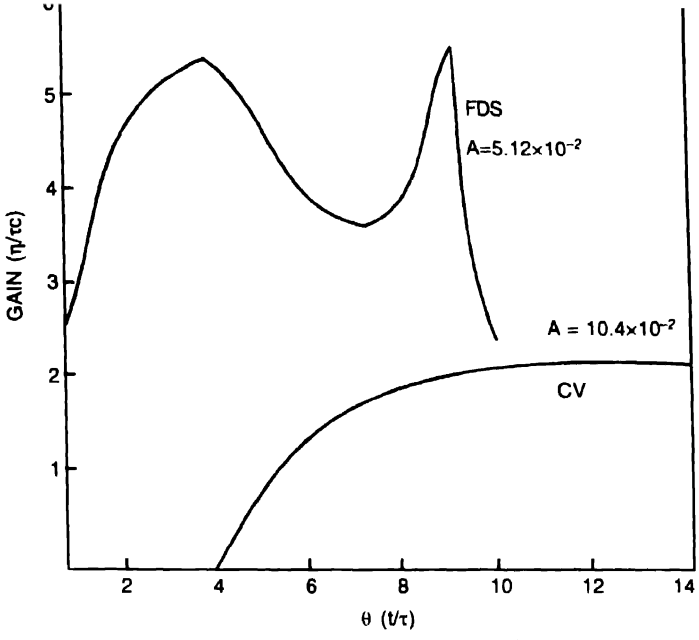

Figure 3 Curves showing the temporal dependence of gain for FDS and CV under optically thin approximation The curves are drawn for A = 5 12 × 10 ' in the case of FDS and A = 10 4 × 10⁻² in the case of CV The gain is shown in terms of (η/τ_c)

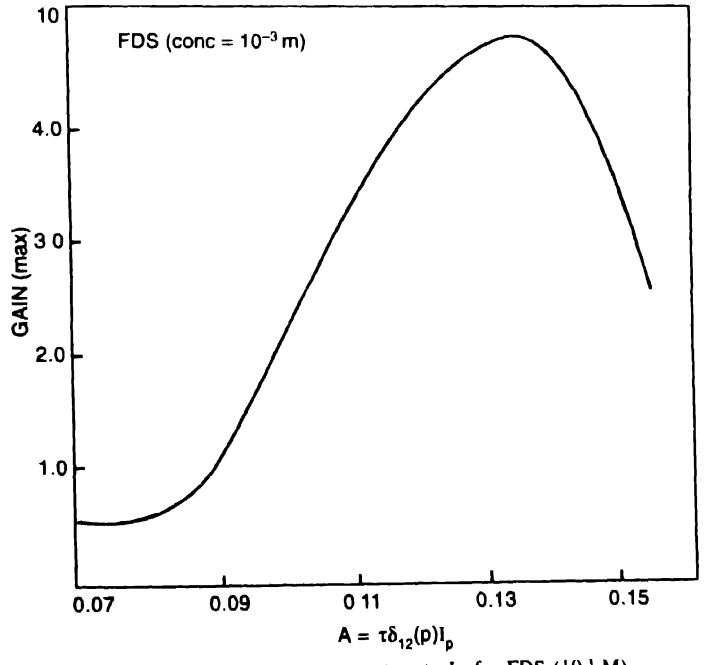

Figure 4. Plot of gain (max) *vs* pump intensity Ip for FDS (10 ' M)

of CV. Our results therefore confirm the different behavior of these dye systems and give substantial support to experimental results.

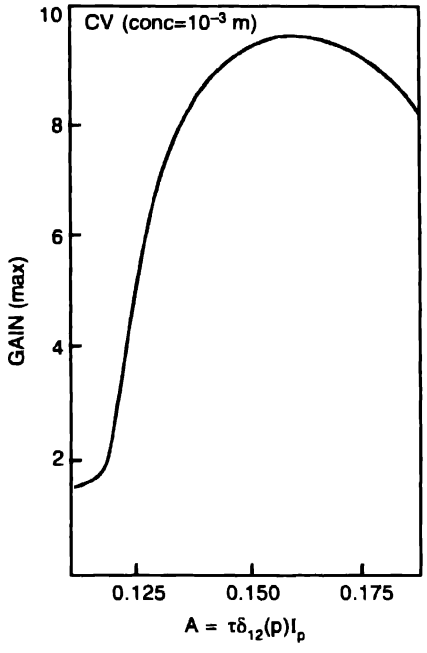

Figure 5 Plot of gain (max) *vs* pump intensity Ip for CV (10^{-3}M)

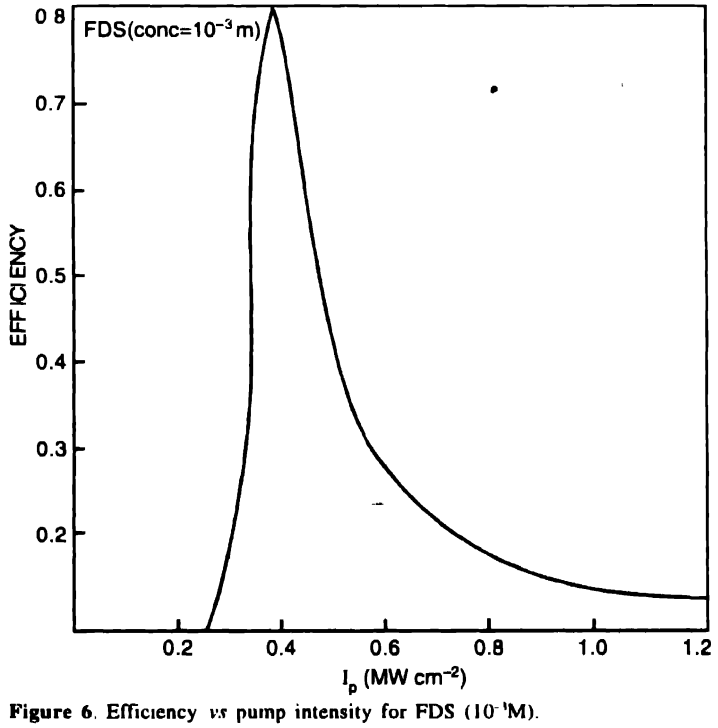

Figure 6. Efficiency *vs* pump intensity for FDS (10^{-3}M).

4. Dependence of efficiency of pump power

The efficiency in defined as $\varepsilon = I_L(\max)/I_p$, where $I_L(\max)$ is the intensity from the dye solution when its full length is exposed to the exciting pulse is the appropriate parameter to be studied when one deals with dye systems. Hence, the study on the variation of ε *vs.* I_p in FDS and CV has been performed. The curves (Figures 6 and 7) show that the peak efficiency is at lower pump intensity for FDS compared to that of CV. Hence for FDS, photoquenching takes place at lower laser intensity than that for CV.

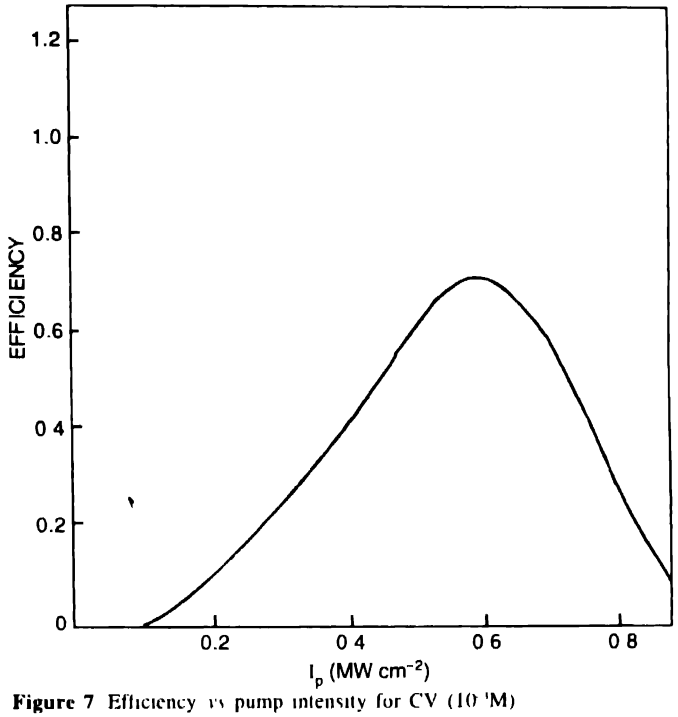

Figure 7 Efficiency vs pump intensity for CV (10^{-5} M)

Our results are found to be consistent with the experimental findings reported [6]. The analysis of the dual spectrum in the above reference gives the twist barrier for TICT formation be around 0.05 eV. The energy scale of the TICT state is estimated to (~ 2.5 eV) in the vicinity of the first excited singlet state. The TICT formation in FDS is described by Taneja *et. al.* [12] based on the nanosecond time resolved fluorescence measurements. The TICT conformation is also studied and established in a number of other non-rigid dyes [8, 13, 14]. In these compounds two aromatic moieties are linked by a single bond and excited state rotation relaxation occurs towards a twisted conformation, coupled with intra molecular electron transfer. The energy of the TICT states is governed by the ionization potential and electron affinity (oxidation and reduction potentials of the sub systems) [15].

5. Conclusions

In this report, we have reanalyzed the experimental study of photoquenching effect in CV and FDS dyes theoretically. The theoretical approach has been applied in an optically thin approximation and the study helps in ascertaining the rigid and non-rigid behavior of the samples. The photoquenching mechanism is found to be effective in both the dyes. However,

FDS shows the TICT due to its non-rigid behavior which also adds to the quenching process. The efficiency *vs.* pump power study shows that the effect becomes more prominent in FDS at relatively lower intensities than that for CV. The slight variations in the theoretical and experimental curves for gain and efficiency *vs.* pump power may be due to the optical loses which is not considered in the calculations. The optically thin approximation is a powerful tool in dealing with the photophysical processes occurring in dye systems.

References

[1] J A Mayer, L L Johnson, E Kierstead, R D Sharma and I Itzkan *Appl. Phy. Lett* **16** 13 (1970)

[2] B B Snavely *Proc IEEE* **57** 1374 (1969)

[3] I Wieder *J Appl Phys Lett* **21** 318 (1972)

[4] S Speiser, F Van der Werf and Kominandeur *J Chem Phys.* **1** 297 (1973)

[5] George C Chennattucherry, G Ajith Kumar and N V Unnikrishnan *Pramana* **43** 237 (1994)

[6] Arun Gaur, L Thaneja, A K Sharma, D Mohan and R D Singh *Optics Commun* **83** 235 (1991)

[7] S Speiser *Chem Phys* **6** 479 (1974)

[8] Latesh Taneja, A K Sharma and R D Singh *J Lumin.* **63** 203 (1995)

[9] D Mohan, Arun Gaur, A K Sharma and R D Singh *Indian J Pure Appl Phys* **28** 315 (1990)

[10] S Speiser and A Bromberg *Chem Phys* **9** 191 (1975)

[11] A Yariv *Quantum Electronics*, (John Wiley & Sons) III Edn p 136 (1989)

[12] L Taneja, A K Sharma and R D Singh *Materials Sci Forum* **223-224** 325 (1996)

[13] V Masilamani, V Chandrasekhar, B M Sivaram, B Sivasankar and S Nadaraj *Opt Commun* **59** 203 (1996)

[14] V Masilamani, D Sastikumar, S Natarajan and P Natarajan *Opt Commun* **62** 389 (1987)

[15] Wolfgang Rettig *Fluorescence Spectroscopy* ed Otto S Wolfbeir (Berlin Springer-Verlag) (1992)